



Studies of Oxide Film Growth / Oxide-Metal Interface Processes via *In Situ/Ex Situ* Analytical Techniques

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SCIENTIFIC ACHIEVEMENT

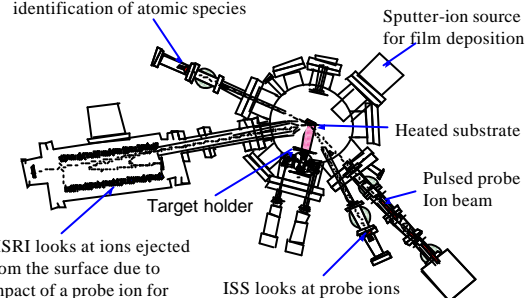
A set of related pulsed ion beam surface analysis methods, known collectively as time of flight ion scattering and recoil spectroscopy (TOF-ISARS) have been used in conjunction with complementary X-ray photoelectron spectroscopy to perform *in situ* studies of oxide film growth and oxide-metal interface processes with nanoscale resolution. The integrated analytical techniques provide surface compositional and structural information on a time scale that is commensurate with thin film deposition and/or surface and interface processes such as oxidation. The techniques are compatible with the geometric constraints of the deposition process and the temperatures and ambient gas pressures required by physical-vapor deposition of thin films and interface processing in relatively high-pressure environments. We have used time-of-flight mass spectroscopy of recoil ions (TOF-MSRI) and X-ray photoelectron spectroscopy (XPS) as *in situ* probes to characterize complex oxide heterostructures. Specifically, we studied growth and free surface oxidation of ferroelectric thin films and oxygen diffusion barrier layers (TiAl, TiAlN) to understand ferroelectric perovskite film growth and barrier oxidation processes when exposing the barrier layers to high temperature (200-700 °C) in oxygen atmospheres. In this poster we show only the work on diffusion barriers. The increase in secondary ions intensity correlates with the surface oxidation. MSRI analysis revealed that amorphous TiAl and TiAlN layer do not get oxidized during free surface oxygen annealing up to 600 °C. XPS confirmed the MSRI results by revealing the existence of a metallic Ti peak in Ti-Al layer. In the case of TiAlN, XPS revealed the formation of TiO₂ at 650-700 °C by replacement of nitrogen chemically bonded to Ti by oxygen atoms. Additional studies were performed to understand the nature of conductive La_{0.5}Sr_{0.5}CoO₃ (LSCO) oxide / TiAl or TiAlN layers. Electrical characterization demonstrated that the LSCO / amorphous TiAl heterostructure exhibit ohmic behavior, while the LSCO / crystalline TiAl one exhibit non-ohmic behavior, mainly due to the formation of an Al₂O₃ interface layer between LSCO and TiAl, induced by grain boundary segregation of oxygen through the crystalline TiAl layer.

SIGNIFICANCE

As thin film thickness and feature size in conventional semiconductor or novel hybrid oxide/semiconductor thin film based devices decrease, new thin film materials, device structures, and complex processing conditions are required. The TOF-ISARS technique described in this highlight has been applied to perform nanoscale studies of relevant phenomena associated with film growth and processing conditions critical to the fabrication of a new generation of advanced semiconductor and hybrid oxide/semiconductor thin film-based devices. The integrated TOF-ISARS/XPS system developed at ANL provides unique insights into fundamental film growth and interface processes that help to develop new materials integration strategies for the fabrication of novel devices based on ferroelectric thin films integrated with Si substrates. The severity of materials integration problems in complex, multi-material electronic devices, and the significance of TOF-ISARS as a tool for understanding them has been acknowledged by the presentation of the R. A. Bunshah Award by the American Vacuum Society in 1994, and an R&D 100 Award in 1997. There is growing interest in using the unique capabilities of TOF-ISARS to develop materials integration strategies for the fabrication of the next generation of high density non-volatile ferroelectric random access memories (NVFRAMs) and high permittivity dynamic random access memories (DRAMs). TOF-ISARS has already provided critical information for the development of low density NVFRAMs, which are the heart of smart cards currently marketed by several companies worldwide.

Time-Of Flight Ion Scattering Angle-Resolved Spectroscopy (TOF-ISARS)

DRS looks at neutrals ejected from the surface due to impact of a probe ion for nanoscale identification of atomic species

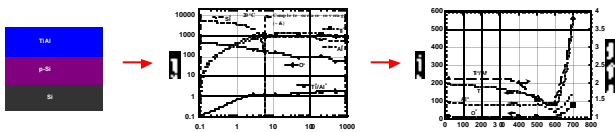


MSRI looks at ions ejected from the surface due to impact of a probe ion for nanoscale identification of atomic species

ISS looks at probe ions scattered from atoms on the surface to identify surface atomic species at the nanoscale

Time-of-flight ion scattering spectroscopy (ISS) and mass spectrometry of recoil ions (MSRI) techniques, developed at ANL, enabled *in situ* studies of film growth and interface processes at pressures 4-7 orders of magnitude higher than in conventional surface analytical techniques

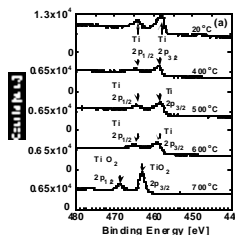
In Situ MSRI Study of Film Growth and Oxidation Processes for a New TiAl Diffusion Barrier



Sputter- deposition of amorphous a-TiAl Diffusion barrier on Si substrate

***In situ* MSRI shows full coverage of Si substrate at about 9 Å of TiAl layer growth (Si signal falls to zero; Ti & Al signals reach saturation)**

***In situ* MSRI shows that amorphous TiAl layer does not oxidize (Ti/Al peak do not increase) until > 600 °C in oxygen**



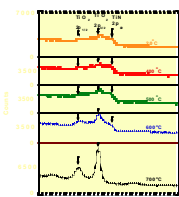
***In situ* XPS analysis confirms that an amorphous TiAl layer oxidizes at > 600 °C via segregation of a Ti nano-layer on the surface and TiO₂ formation**

In Situ MSRI / XPS Study of Oxidation Processes for a TiAlN Diffusion Barrier



Sputter- deposition of amorphous a-TiAlN diffusion barrier on Si substrate

***In situ* MSRI shows that a-TiAlN layer does not oxidize (Ti / Al peak do not increase) until between 500-600 °C in oxygen**

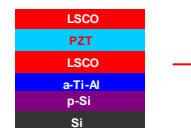


XPS analysis shows partial TiO₂ formation on as-deposited TiAlN layer. The Ti 2p peak shows a chemical shift characteristic of TiN for a virgin surface

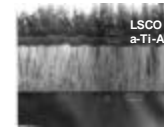
XPS analysis shows O peak intensity increase, correlated with the transformation of the TiAlN surface into TiO₂ for temperatures > 600 °C

XPS analysis shows N peak disappearance from the N spectrum for subst. temperatures > 600 °C, correlating with the O peak increase in the O spectrum, indicative of N replacement by O in bond to Ti

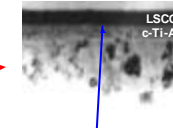
Ex Situ Cross-Section TEM Characterization of LSCO/ PZT/ LSCO / amorphous a-TiAl and crystalline c-TiAl Heterostructures



Conductive oxide La_{0.5}Sr_{0.5}CoO₃ electrode is grown on a-TiAl layer followed by PZT / LSCO electrode to complete the ferroelectric capacitor on Si

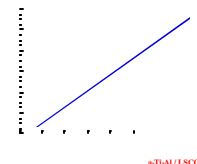


***Ex situ* cross-section TEM reveals sharp/clean interfaces in LSCO/PZT/ LSCO/a-TiAl hetero-structure capacitor on Si**



***Ex situ* cross-section TEM reveals a segregated layer (Al₂O₃) at the LSCO/crystalline c-TiAl interface in a LSCO/ PZT/LSCO/c-TiAl hetero-structure capacitor on Si.**

Electrical Characterization of LSCO/a-TiAl and c-TiAl Heterostructures



Ohmic behavior of the a-TiAl/LSCO heterostructure consistent with a clean/ sharp interface

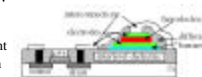
c-TiAl/LSCO

Non-linear behavior consistent with dielectric breakdown due to an insulating oxide (i.e., Al₂O₃) formed at the LSCO/ c-TiAl interface via grain boundary-dominated oxygen segregation to the interface

Remanent Polarization: ~ 28 μC/cm² (at 5 V)

Coercive Voltage: ~ 1V

Capacitors exhibited excellent fatigue, imprint and logic state retention properties



***Ex situ* electrical characterization of LSCO/ PZT/ LSCO/a-TiAl capacitor on Si shows excellent ferroelectric properties for application to NVFRAMs**

CONCLUSIONS

Complementary *in situ* and *ex situ* characterization of ferroelectric/diffusion barrier heterostructures provided unique insights into physical phenomena and electrical properties of LSCO/ PZT/ LSCO/a-TiAl capacitors on Si and demonstrated that these capacitors exhibit excellent ferroelectric properties for application to NVFRAMs

FUTURE WORK

- *In situ* TOF-ISARS/XPS studies and complementary *ex situ* TEM and electrical characterization of :
 - high-dielectric constant thin films / silicon interfaces
 - perovskite ferroelectric / diffusion barrier / copper heterostructure interfaces
- Assembly of 3rd generation oxide film deposition system (including ion beam sputter-deposition and molecular beam epitaxy) integrated with TOF-ISARS, RHEED, and Spectroscopic Ellipsometry for studies of oxide thin film heterostructures at the nanoscale

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